

# **Course „Nanopartikel in der Umwelt“ - Natural NP (NNP) and colloids in waters and soils**

Inorganic NNP

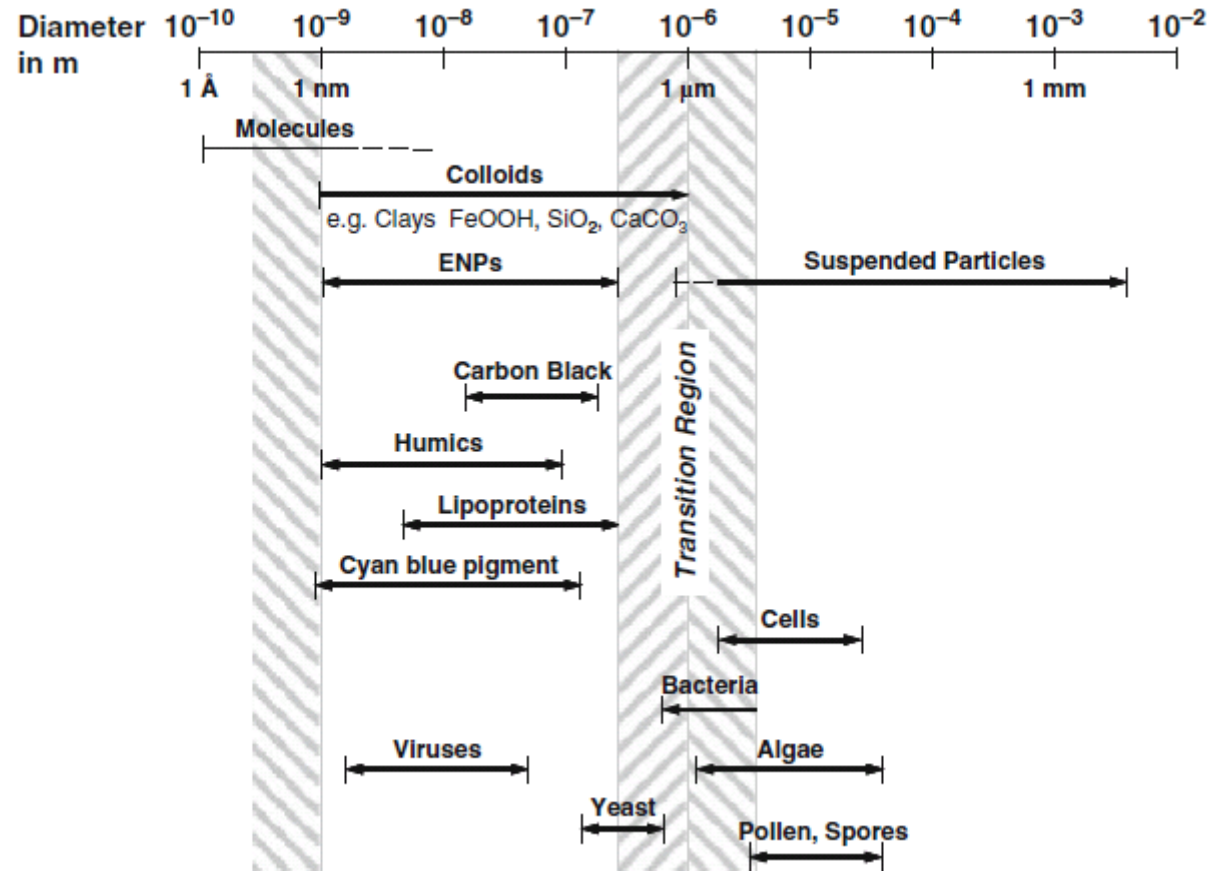
Organic NNP

Sources and sinks

Heteroaggregates

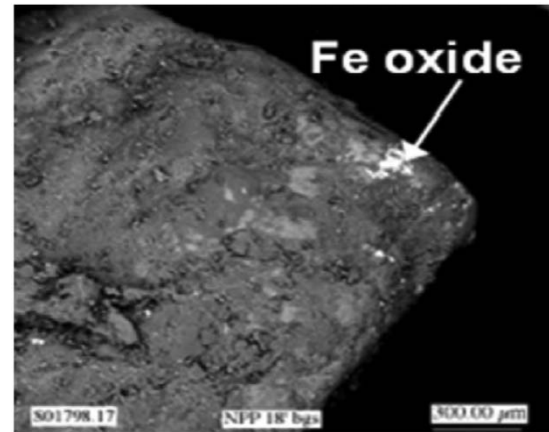
Stability

# Size ranges for ENP and colloids in aqueous systems

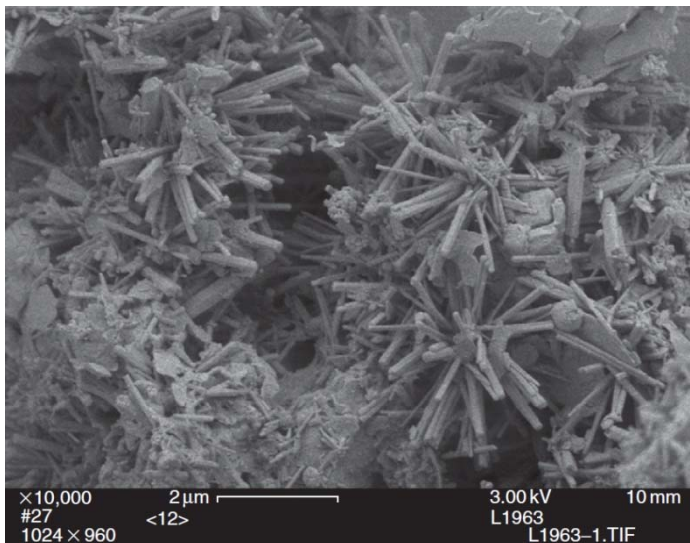


# Nanoparticles – Three classes in terrestrial ecosystems: nanofilms (or nanosheets), nanorods, and NPs

**Nanosheets** in the form of thin coatings on surfaces of primary minerals.  
A small Fe-oxide coating on the surface of a feldspar particle from a sediment

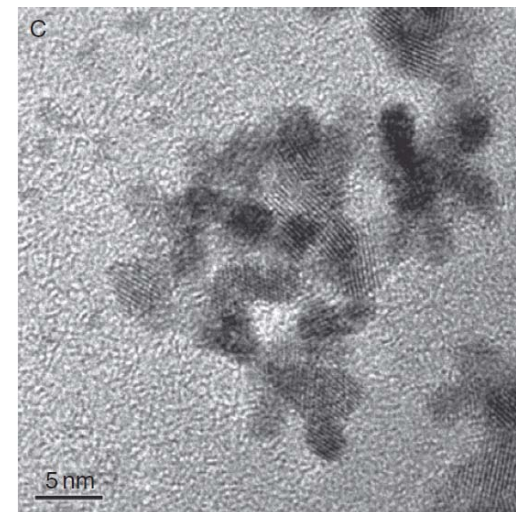


**Nanorods:** Sodalite [ $\text{Na}_4\text{Al}_3(\text{SiO}_4)_3\text{NO}_3$ ] precipitated out of solution that became supersaturated as a result of dissolution of soil minerals



(Hochella et al., 2008)

**Particles:** TEM image of biogenic uraninite ( $\text{UO}_2$ ) NPs, a product of microbial U(VI) reduction by a soil bacterium *Shewanella* sp.



# Nanoparticles – ubiquitous in the natural environment



FeOOH

- in waters



FeO

FeS

- in soils and sediments

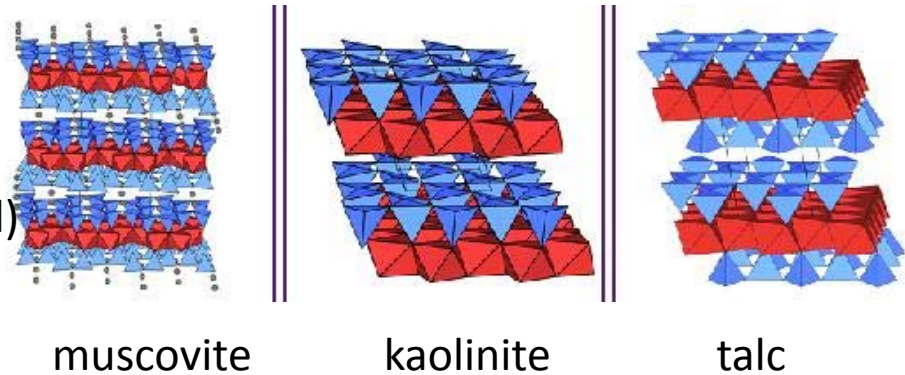
Dominant phases include:

- Clay minerals (hydrated aluminosilicates of K, Mg, Fe etc.)
- Aluminium oxides/hydroxides
- Iron and manganese oxides/hydroxides
- Silica
- Nanoscale aggregates of NOM
- Bacterial appendages

## PHYLLOSILICATE (clay mineral) classification

The phyllosilicates are classified based upon:

1. the number of tet. and oct. in a sheet
2. the octahedral site occupancy (di or trioctahedral)
3. charge per formula unit for each layer.



### General Classes (layer build-up) of Phyllosilicate Minerals:

Layer Type	Charge <sup>†</sup>	Trioctahedral	Diocahedral
1 octahedra	0	brucite, $Mg(OH)_2$	gibbsite, $Al(OH)_3$
1 tet. : 1 oct.	0	serpentine, $Mg_3Si_2O_5(OH)_4$	kaolinite, $Al_2Si_2O_5(OH)_2$
2 tet. : 1 oct. $Al_2Si_4O_{10}(OH)_2$	0	talc, $Mg_3Si_4O_{10}(OH)_2$	pyrophyllite, $Al_3Si_4O_{10}(OH)_2$
2 tet: 1 oct.	1	phlogopite $KMg_3(AlSi_3O_{10})(OH)_2$	muscovite $KAl_2(AlSi_3O_{10})(OH)_2$
	1	biotite $KFe_3(AlSi_3O_{10})(OH)_2$	
	0.6-0.8	illite (hydrous mica) $K(Na,Ca) Al_{1.3}Fe_{0.4}Mn_{0.2}Si_{3.4}Al_{0.6}O_{10}(OH)_2$	
	0.6-0.9		vermiculite
	0.25-0.6		smectite

<sup>†</sup> The layer charge per formula unit

## Clay minerals and their properties

**Brucite and Gibbsite:** Gibbsite is a common secondary mineral, abundant in well-weathered soils such as Oxisols. Brucite is less commonly observed in soils (weathers rapidly).

**Kaolinite:** The structural sheets composed of 1 tet. to 1 oct. are held together by H-bonds. Because of the numerous bonds these sheets are held rather tightly together and are thus not expandable. Probably the most ubiquitous silicate mineral in soils

- SA is also low, 7 to 30 m<sup>2</sup>/g
- low cation exchange capacity: 5-15 cmol/Kg
- charge from unsatisfied bonds ==> pH dependent

**Illite (hydrous mica):** “nonexpanding, dioctahedral, K-bearing mica-like minerals”

- $\approx \text{KAl}_1.3\text{Fe}_0.4\text{Mg}_0.2\text{Si}_3.4\text{Al}_0.6\text{O}_{10}(\text{OH})_2$
- layer charge: 0.6 - 0.8 per formula unit
- derived from the weathering of the muscovite
- divalent cation substitutes in the octahedral layer for Al
- quantity of Si is increased in the tetrahedral layer
- CEC is approximately 30 cmol / Kg (30 meq/100g)
- high affinity for K, Cs, and NH<sub>4</sub><sup>+</sup>

### Smectites:

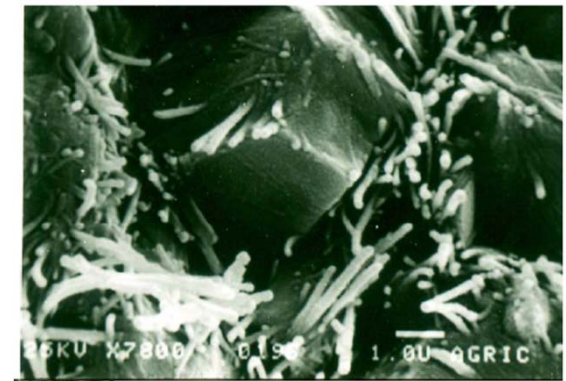
- Most expandable of the clay minerals ☐ shrink-swell properties in soils
- Very high water holding capacity as a result of such swelling
- Most common smectite:

**Montmorillonite:**  $\text{M}_y \cdot n\text{H}_2\text{O} (\text{Al}_{2-y}\text{Mg}_y)(\text{Si}_4\text{O}_{10}(\text{OH})_2$   $y = 0.25$  to  $0.45$

\*commercially available and known as “bentonite” clay.

- CEC ranges from 800 to 1200 mmol / Kg with a surface area of 600-800 m<sup>2</sup>/g.
- variable charge a minor component of mineral edges

### ...another clay minerals...



**Palygorskite fibers on calcite crystals**

## Oxides and hydrous oxides and their properties

### Aluminum Oxides:

- Most abundant of the secondary minerals is gibbsite,  $\text{Al}(\text{OH})_3$ .
- Very stable mineral at low temperatures and is the building block for other phyllosilicates (the dioctahedral class)
- SA of gibbsite, 5 – 20 m<sup>2</sup>/g
- Hexagonal sheets are bound by van der Waals bonds
- ubiquitous in well developed soils
- Al-oxides have high ZPC that ranges from 8 to 9.5.

**Iron Oxides:** Ferric hydrous oxides are abundant in many soils and due to their strong pigmentation they are easily recognized; the yellow and red soil colors are due to this class of minerals. Based on radius ratios, Fe(III) should enter octahedral coordination, and this is observed in nature. Accordingly, the Fe oxides are similar to the Al-oxides.

- **Ferrihydrite:**  $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$  (n = 5 to 9, usually): an amorphous iron hydroxide.
- **Goethite** ( $\alpha\text{-FeOOH}$ ) is the most abundant of the iron oxides
  - yellowish color
- **Hematite** ( $\alpha\text{-Fe}_2\text{O}_3$ )
  - bright pink color
  - favored in high temperature low moisture areas
  - high pH favors the formation of hematite relative to goethite
- Form concretions and coatings in many soils

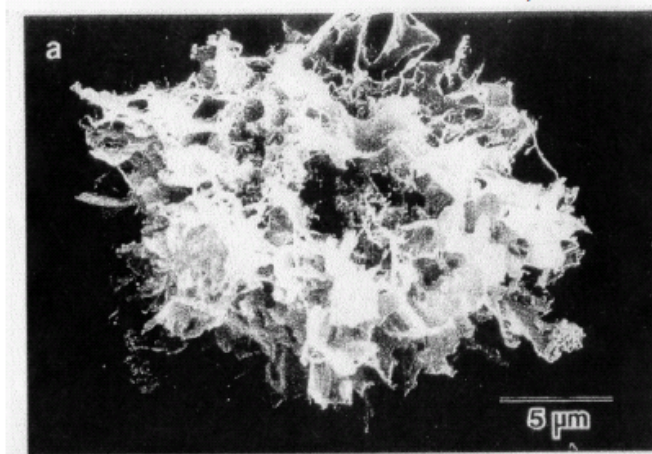
### Manganese Oxides:

- MnO<sub>2</sub>
- Very reactive; high sorption capacity
- Very strong oxidants
- Form black coatings or nodules

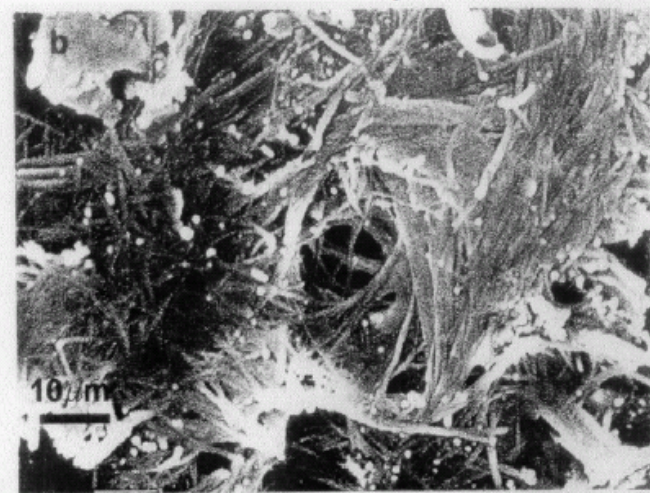
# Manganese oxide nanomaterials

- a. Birnessite (cultured), b. todorokite (siderite coating),  
c. todorokite (soil), and d. lithiophorite (Oxisol, macro particle)

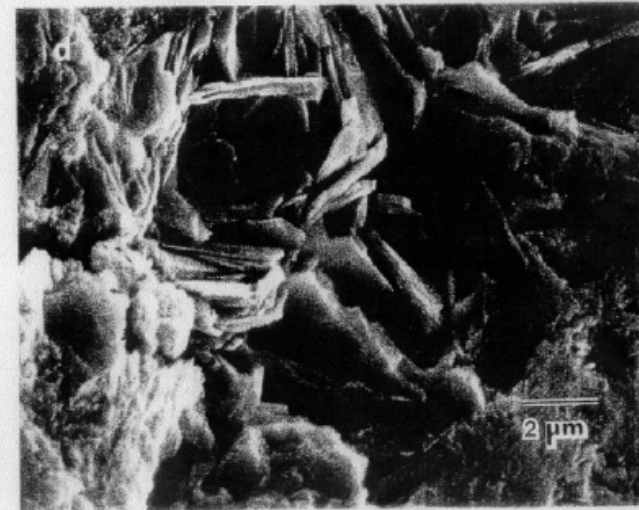
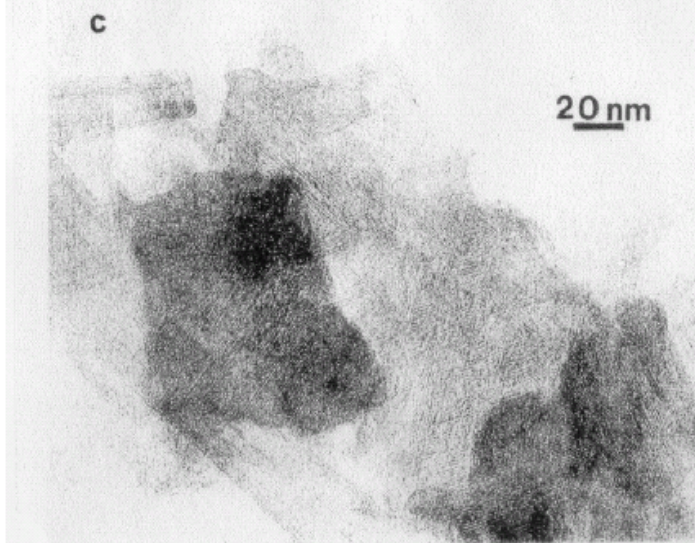
Golden et al., 1992



Senkayi et al., 1986



Golden et al., 1993





## Characteristics of Inorganic Colloids/Nanoparticles

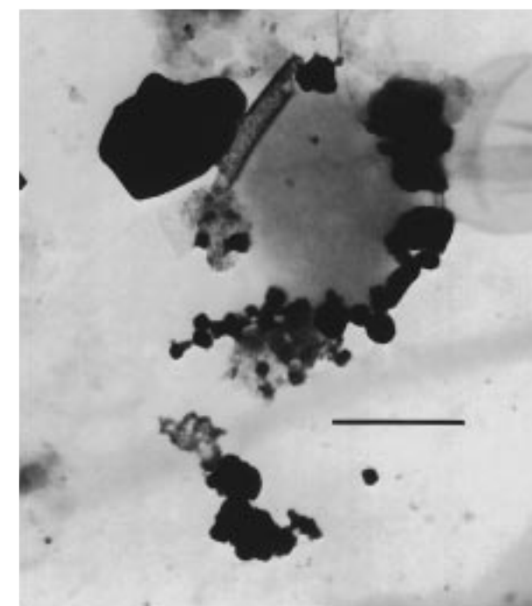
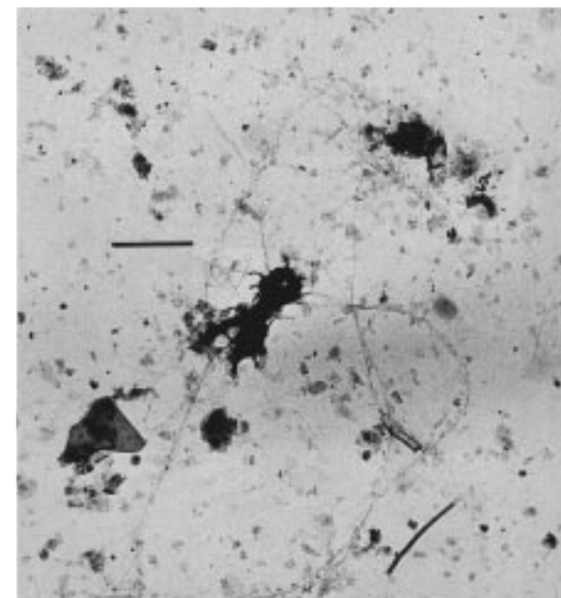
Buffle et al., 1998

nature of solid	pH <sub>ZPC</sub>	site density <sup>c</sup> (nm <sup>-2</sup> )	specific surface area (m <sup>2</sup> g <sup>-1</sup> )
am-SiO <sub>2</sub>	3.0–3.5	4.5–12	40–260
am-FeOOH	7.9–8.1	0.1–0.9 mol/ mol of Fe	160–700
am-Al <sub>2</sub> O <sub>3</sub>	≈9.4	2–12 <sup>d</sup>	
am-MnO <sub>2</sub>	≈2.3	6–20 <sup>d</sup>	260
allophanes		0.4–1.2	500–700
kaolinite	3.3–4.6 <sup>b</sup>	0.6–3.6	10–20
chlorite		0.6–2.4	92–97
illite		0.9–2.7	90–130
smectites	≤2.5 <sup>b</sup>	0.5–1.0	750–800
vermiculites		0.9–1.6	750–800

### TEM images of inorganic colloids and aggregates with NOM

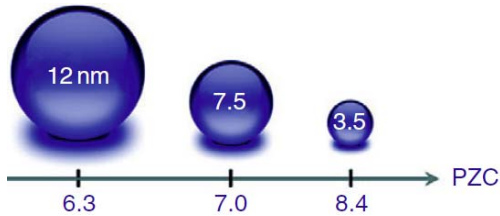
Top: Colloids in the supernatant of mildly centrifuged Rhine River sample (centrifugation eliminates particles larger than a few micrometers). Images show isolated clay colloids and their compact aggregates as well as clay colloids associated within a fibril network. Scale bar corresponds to 1 μm.

Bottom: Compact heteroaggregate from a lake (no fractionation before embedding colloids in resin). The picture shows a spherical silica particle (gray at center) aggregated with smaller iron hydroxide particles (black spheroids), a clay particle, and some biological debris. Scale bar corresponds to 250 nm.

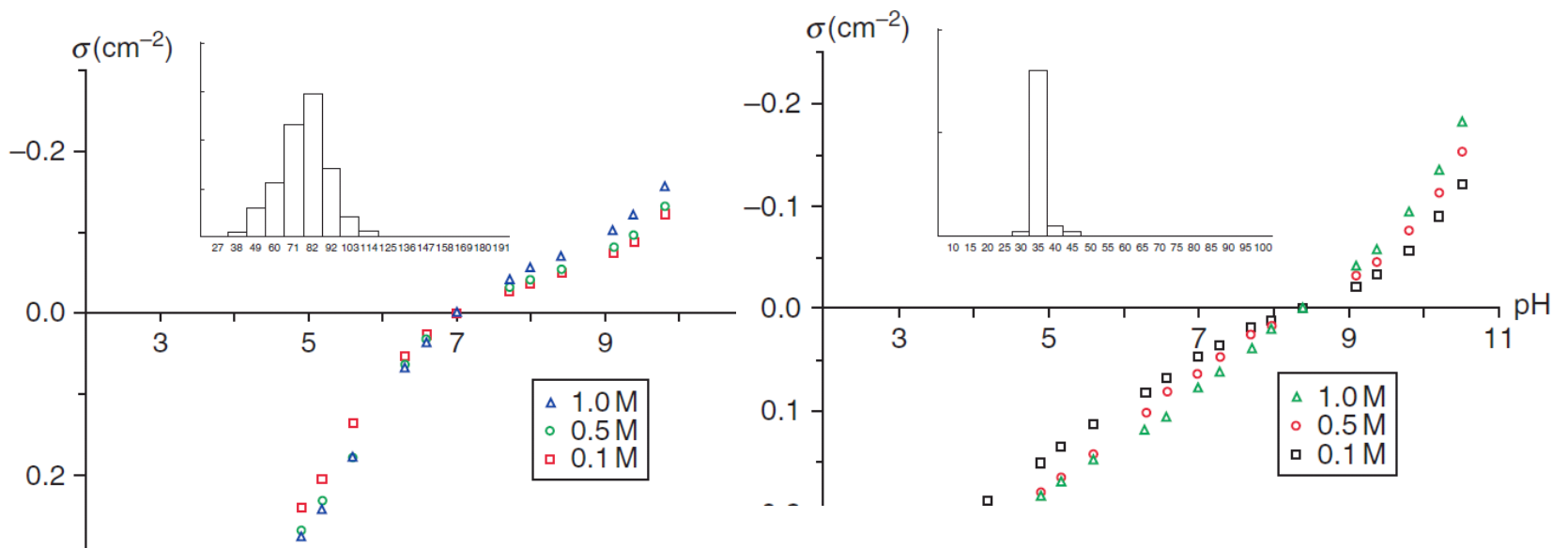


# Nanoscale size-dependent properties

Changes in PZC as a function of particle nano size



Titration diagrams of aqueous suspensions of maghemite consisting of spherical nanoparticles of 7.5 (left), and 3.5 nm (right) in average diameter in NaNO<sub>3</sub> aqueous solutions of various concentrations at 25 C. The single point of intersection of the three titration curves indicates the PZC. The insets show the histograms of size distributions as determined by electron microscopy.



(Vayssieres, 2009)

# Organic Macromolecules

**Dissolved, colloidal and particulate organic matter (DOM, COM, and POM)**

**Natural organic matter (NOM)** can be divided: **humic substances** and **non-humic substances**

**Humic substances:** **humic acids (HA)** – soluble in water at  $\text{pH} > 2$ ,  
**fulvic acids (FA)** – soluble in water,  
and **humins** – insoluble in water

**Non-humic substances:** **proteins, polysaccharides**, nucleic acids, small molecules such as sugars, amino acids

**Extracellular polymeric substances (EPS) – fibrillar polysaccharides**

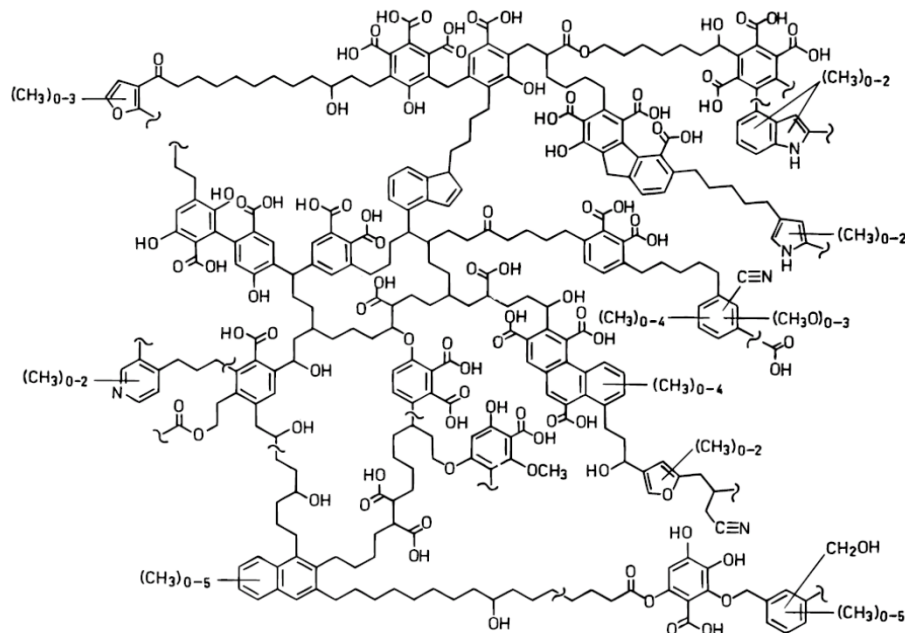
**EPS** - important role in fate of colloids and nanoparticles

NOM: often as surface coating on inorganic colloids/nanoparticles

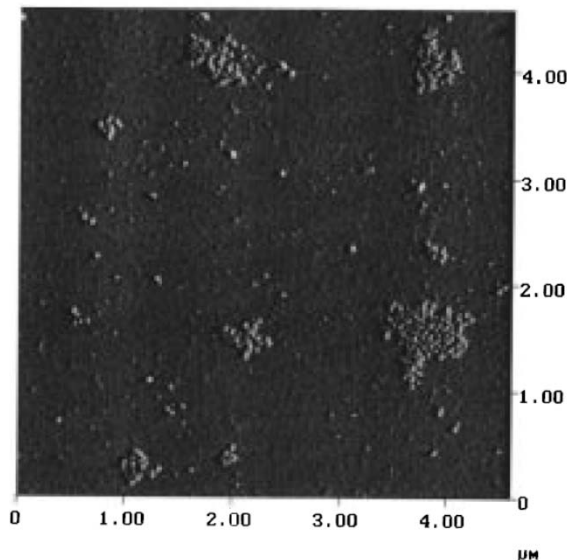
## Characteristics of Major Groups of NOM

nature (origin)	molar mass (Da)	dimensions (nm)	supramolecular structure	electrical charge for fully dissociated sites (mequiv g <sup>-1</sup> )	av age or degradation time
<b>Section A: Rigid Biopolymers (RB)</b>					
mucopolysaccharides, peptidoglycans, hemicellulose, pectic compounds (microbial cell walls + extracellular products) (32–34)	10 <sup>4</sup> –> 10 <sup>5</sup>	thickness: 1–3; length: 100–>1000 (22, 38, 39)	fibrillar structures based on double or triple helix formation (44); sometimes coils or gels depending on nature of cation, pH, or ionic strength (45)	minimum: 0; typically: –0.35 to –0.83; maximum: ~–6	months (surface waters) to centuries (deep waters)
<b>Section B: (Soil-Derived) Fulvic Compounds (FC)</b>					
see Figure 3A for composition (fulvic fraction of soil leached out by rainfall)	500–5000 typically: number average = 2300; weight average = 1000 (6, 35, 36)	Stokes radius = 0.4–1.4 (pH 1–10) (40); gyration radius = 0.5–1.4 (different samples) (41, 42)	spheroids; aggregates of spheroids; occasionally gels (22)	–6 to –11	~450 years in soils
<b>Section C: Flexible Biopolymers (FB)</b>					
aquagenic refractory organic matter (AROM) (recombination of amino acids, sugars, etc. released by plankton)	500–800 (43)		flexible	–2.1 to –5.5 (54)	10–7000 years
reserve polysaccharides (internal cellular content)			flexible		hours to days (6, 34)
proteic compounds	<a few times 10 <sup>4</sup> (37)		flexible		hours to days (6, 34)

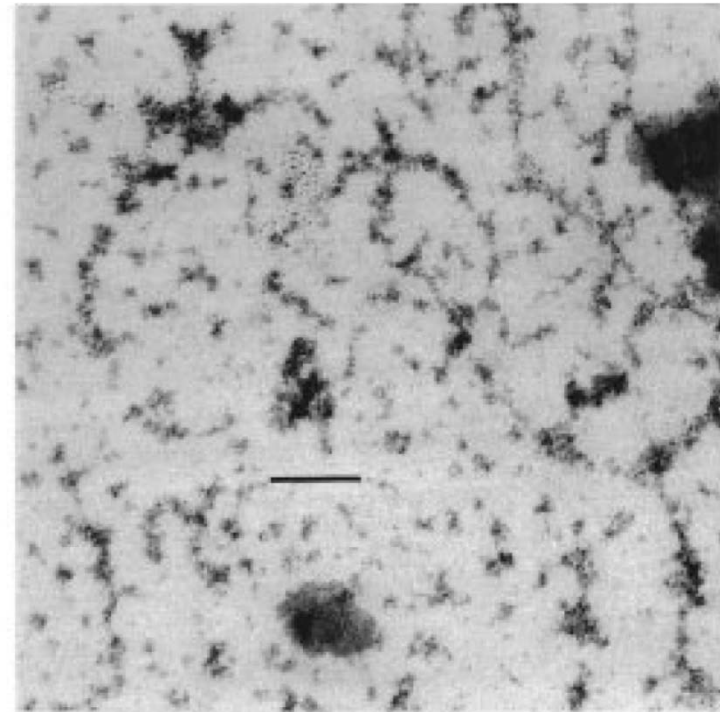
## Proposed chemical formula for fulvic compounds



**AFM image of a soil fulvic compound (pH)6.5; ionic strength)10-2 M) showing isolated FC (individual points) and FC aggregates. The thickness of the adsorbed FC is typically 0.4-2 nm**



**TEM image of FC-rich NOM from a lake sample (pH 7.5; ionic strength 10-2 M). No fractionation was performed prior to embedding in resin. This image is interpreted as having individual FC macromolecules (the smallest black points), homoaggregates (association of black points) and FC associated with fibrillar compounds. Scale bar corresponds to 100 nm.**

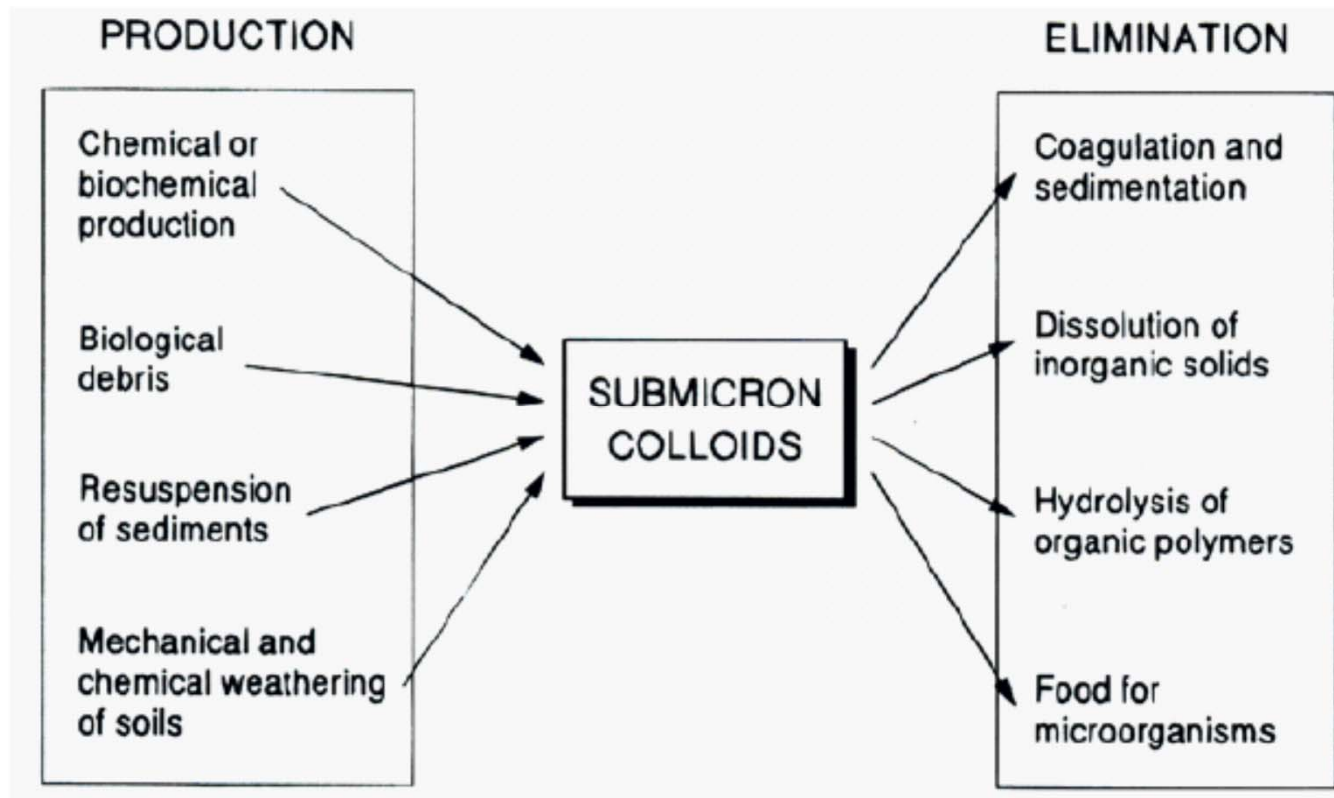


## Physicochemical Parameters of Some Microbially Produced Polysaccharides

compound	molar mass ( $M_w$ ) <sup>a</sup> (kDa)	gyration radius, $R_G$ (nm)	persistence length (nm) <sup>c</sup>	comments
schizophyllan	400–500	NA <sup>e</sup>	130–190	neutral, rigid, rod-like, triple helical structures
xanthan	100–2500	NA	100–140	single- or double-stranded structure; up to two carboxyl groups per five sugar repeating unit
gellan	100–2000	NA	100–140	single-stranded or double-helical structure depending on conditions; negatively charged polysaccharide
alginate	200–2000	110 <sup>b,d</sup>	9	negatively charged polyelectrolytes; extended random coils
dextran	3–2000	20 <sup>b</sup>	2.75	neutral; dense coil

In general polysaccharides are polydisperse with respect to molecular weight since (i) they are not coded for in the DNA of the organism but are synthesized by polymerase enzymes and (ii) during extraction there is substantial depolymerization. For this reason, values given are representative only, designed to give an idea of the natural variations of the molar masses. b) Radius of gyration for molecule of  $M_w$  ) 500 kDa. c) The persistence length corresponds to the length of a statistically straight segment in the polymer chain and gives an indication of the rigidity of the polysaccharide. For example, schizophyllan has a total length of approximately 210 nm of which ca.. 160 nm lies along a single axis. d) Estimated. e) NA, not applicable.

**Main biotic and abiotic sources and sinks that influence the nature and size distribution of natural aquatic colloidal material/nanomaterials**



## Sources of inorganic colloids/nanoparticles

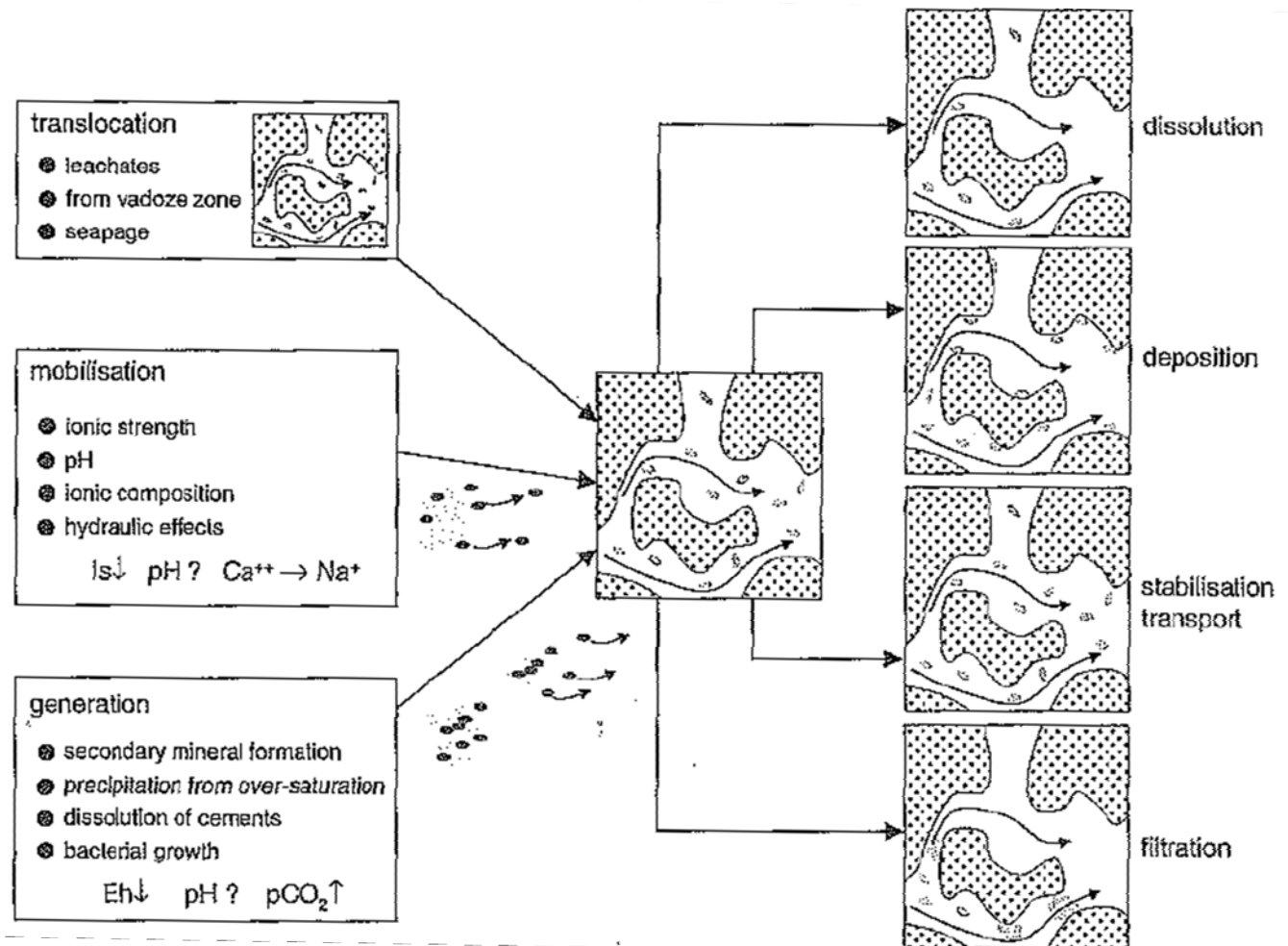
**In surface waters:** Detachment from soil surfaces; sediment resuspension, chemical precipitation; biogenic primarily bacterial origin

**In soils and groundwater:** Detachment from soil surfaces due to changes in solution chemistry; Rain fall or soil irrigation

e.g.:

- Calcite in lakes
- Metal sulfides in anoxic waters
- Fe und Mn oxides in eutrophic lakes

Colloid release:  
high pH, low ionic strength,  
high flow velocity





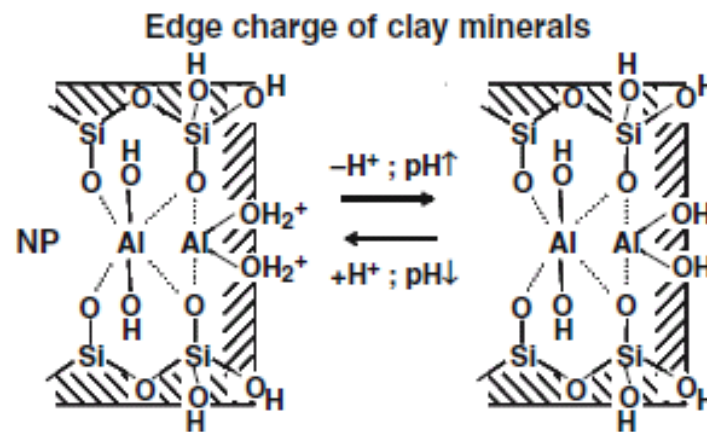
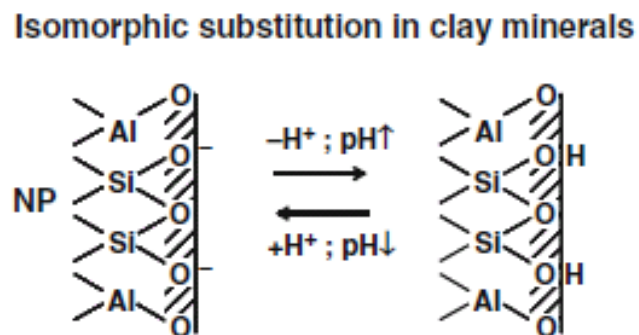
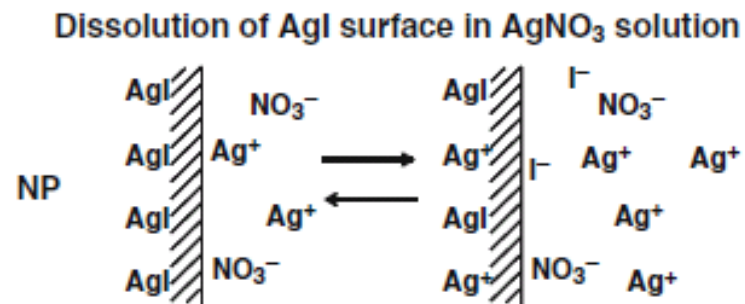
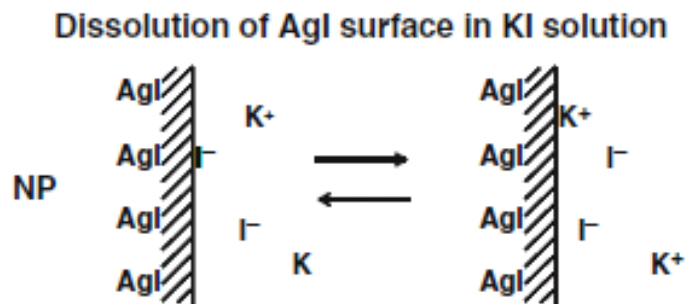
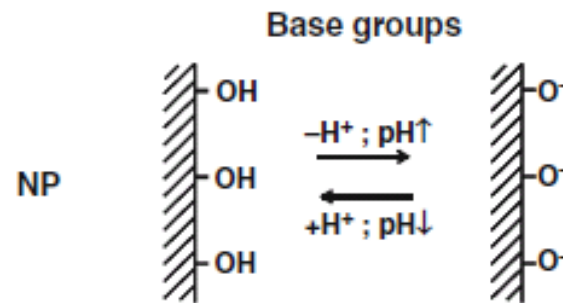
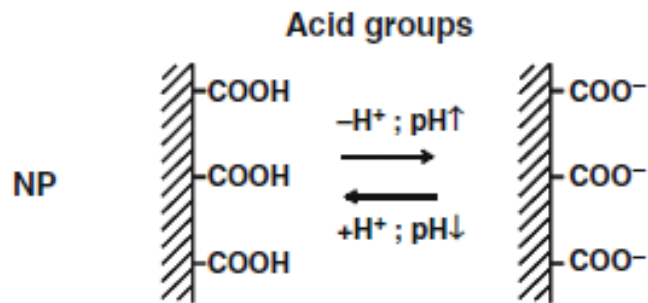
## Transport of (nano)particulate matter - in flowing waters

iron hydroxide precipitate formed on mixing of acid mine waters with dissolved iron and neutral stream waters →

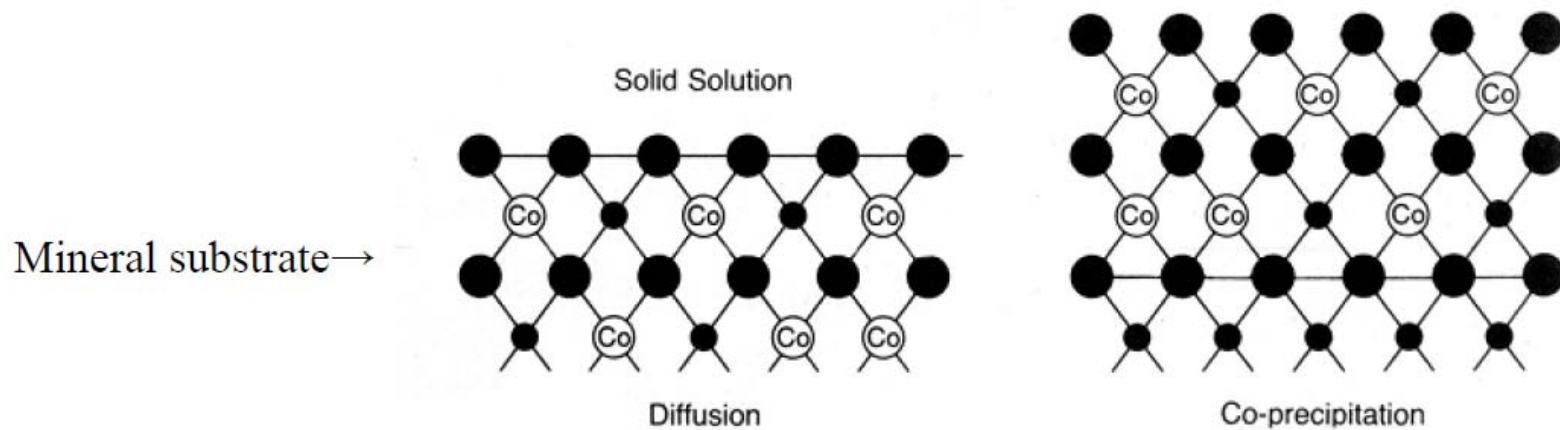
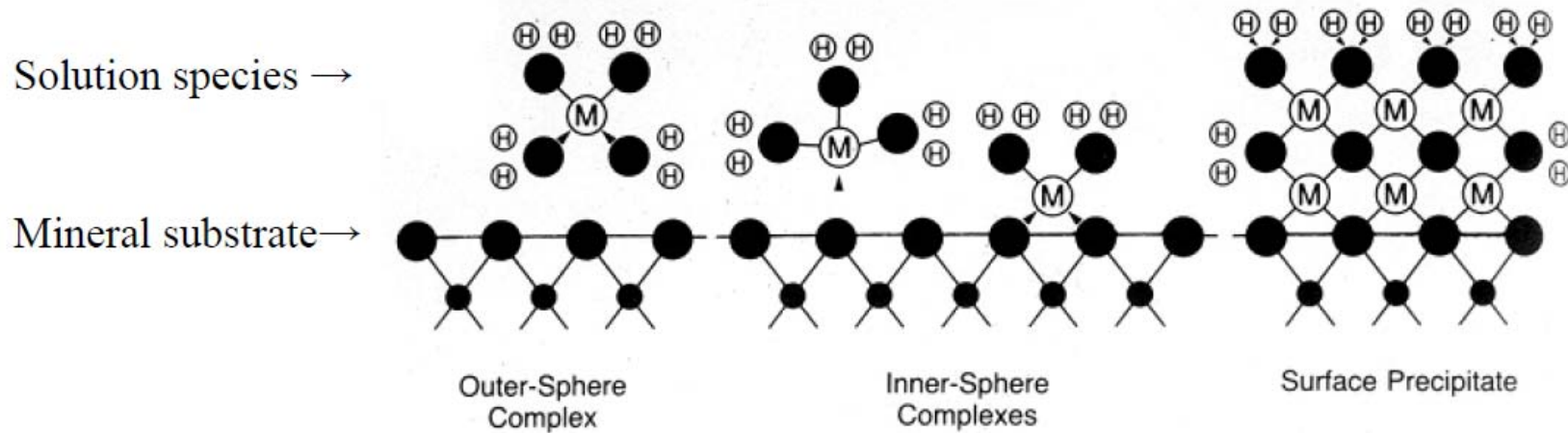


← and subsequent precipitation in estuarine sediments

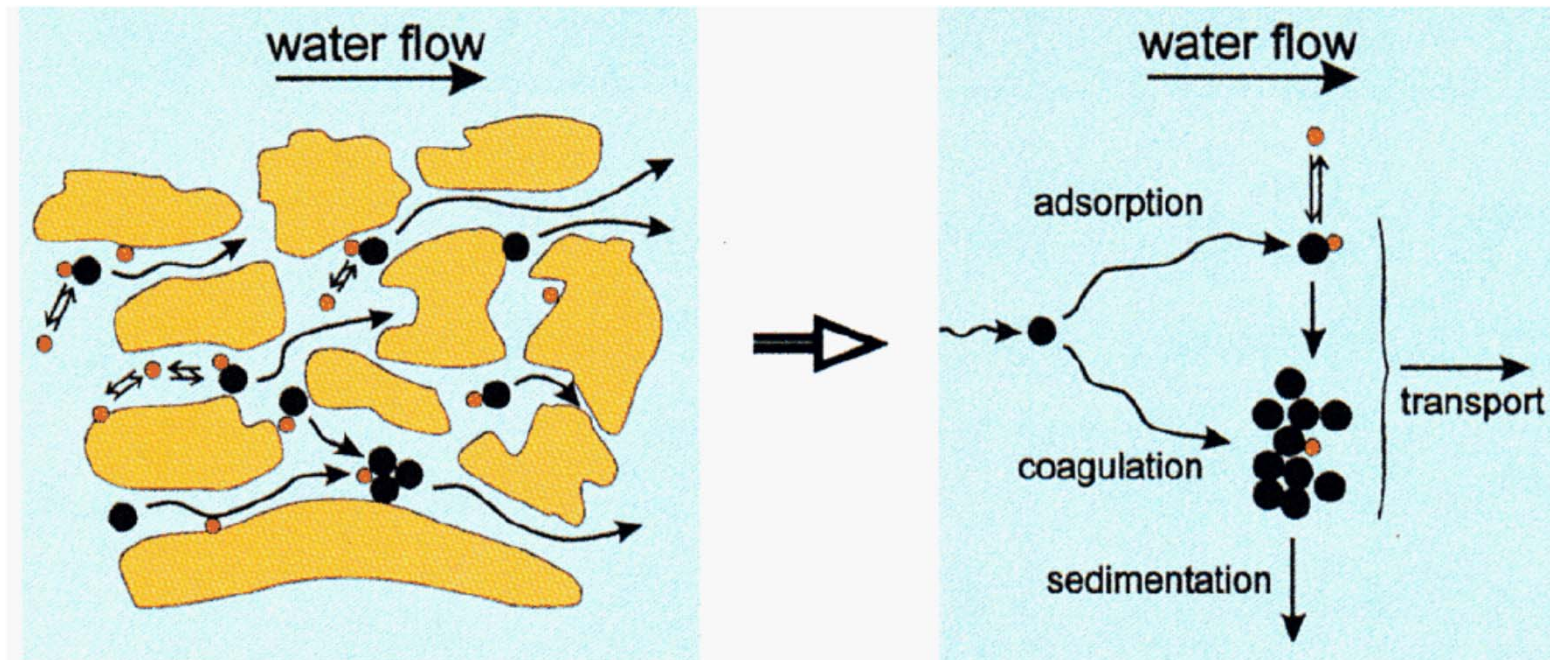
# Surface charges and their generation



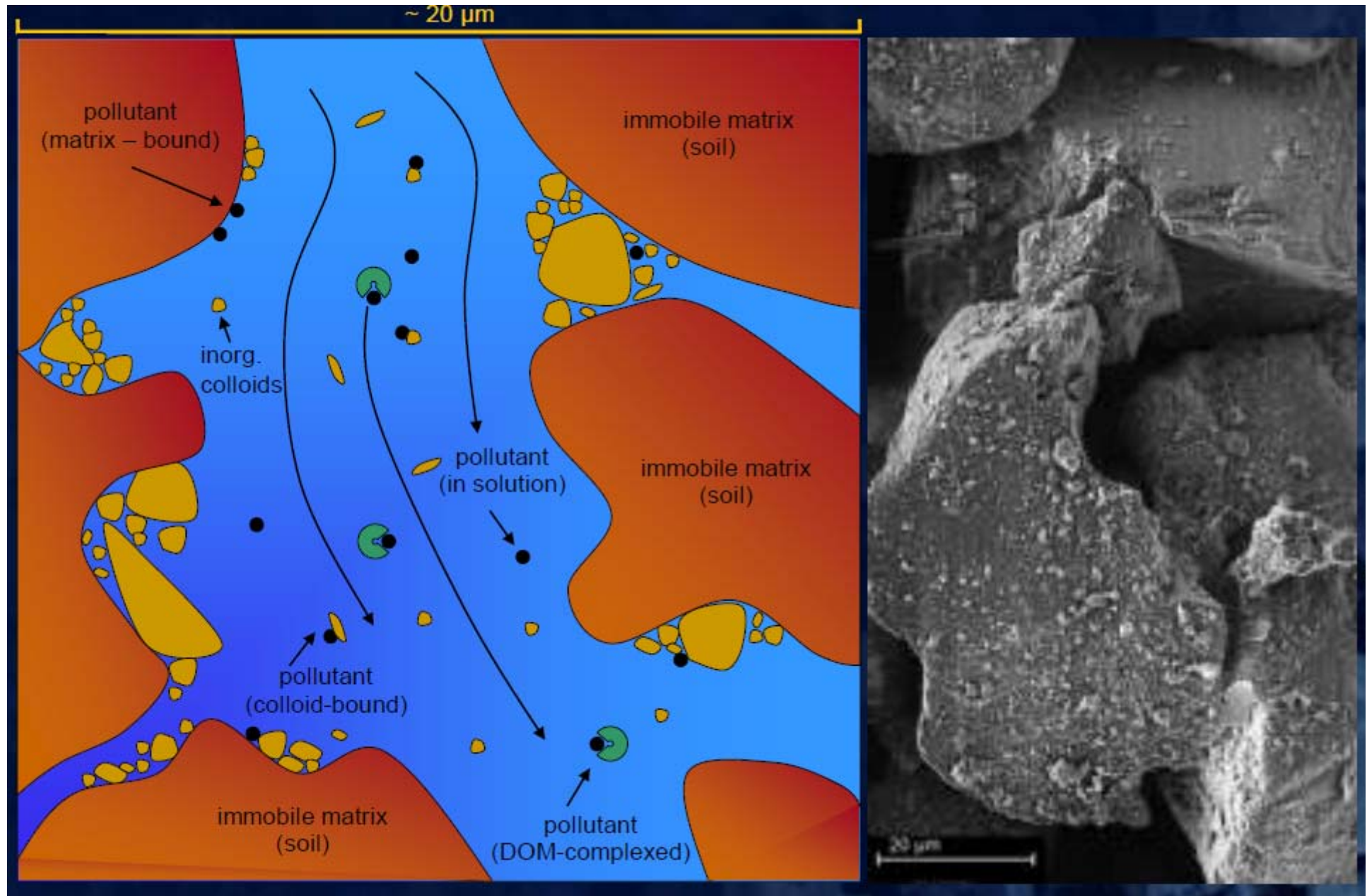
# Reaction of nanoparticle solids with species in solution to form 'sorption' complexes, precipitates or replacing phases



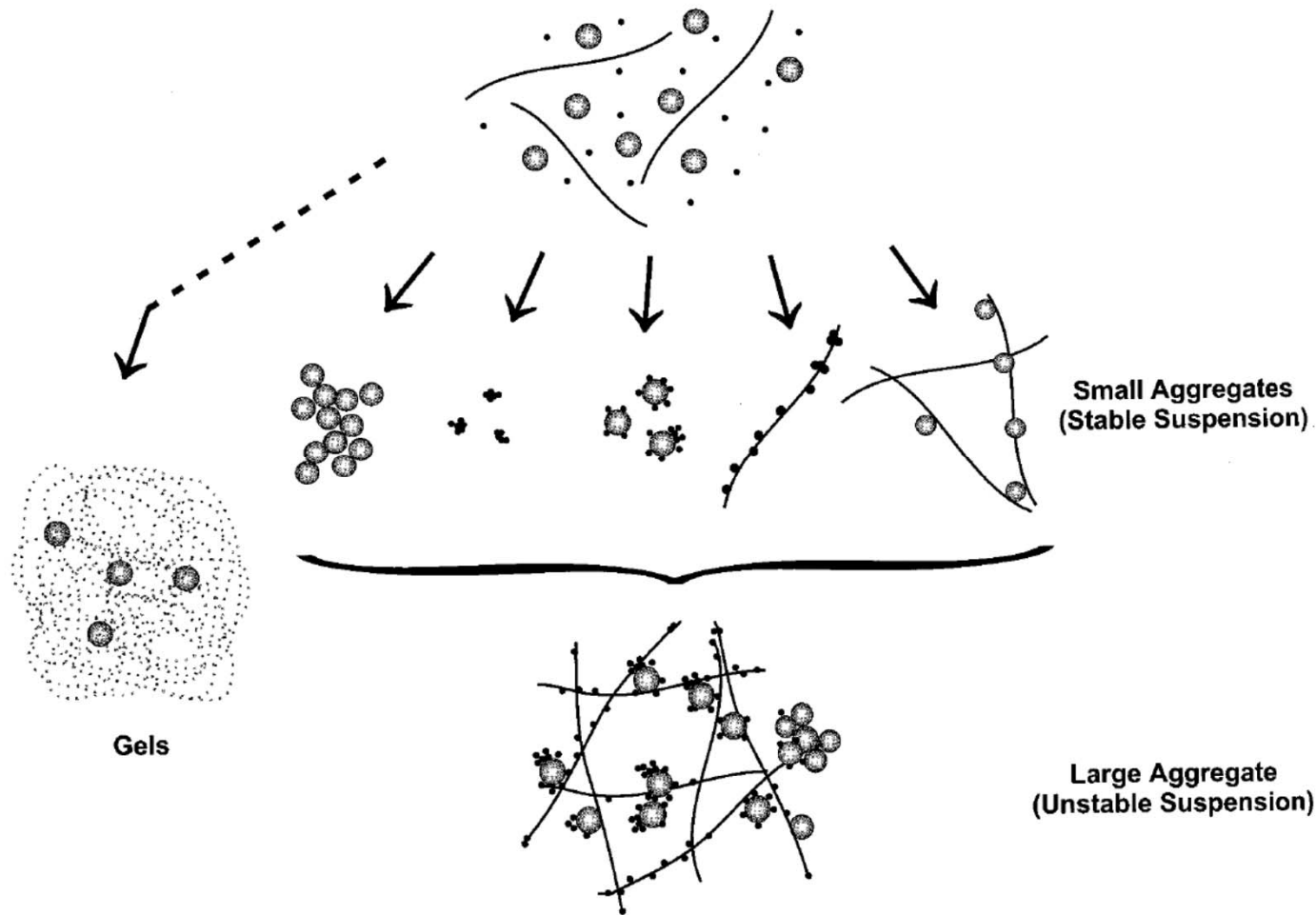
**Co-transport of vital and toxic compounds** (small. red circles) by **colloidal carrier** (large. black circles) in porous media and surface waters. The colloidal carrier may be an inorganic nanoparticle, an organic macromolecule, a biological am (rims, bacterium, picoplankton, biological debris) or an aggregate of these.



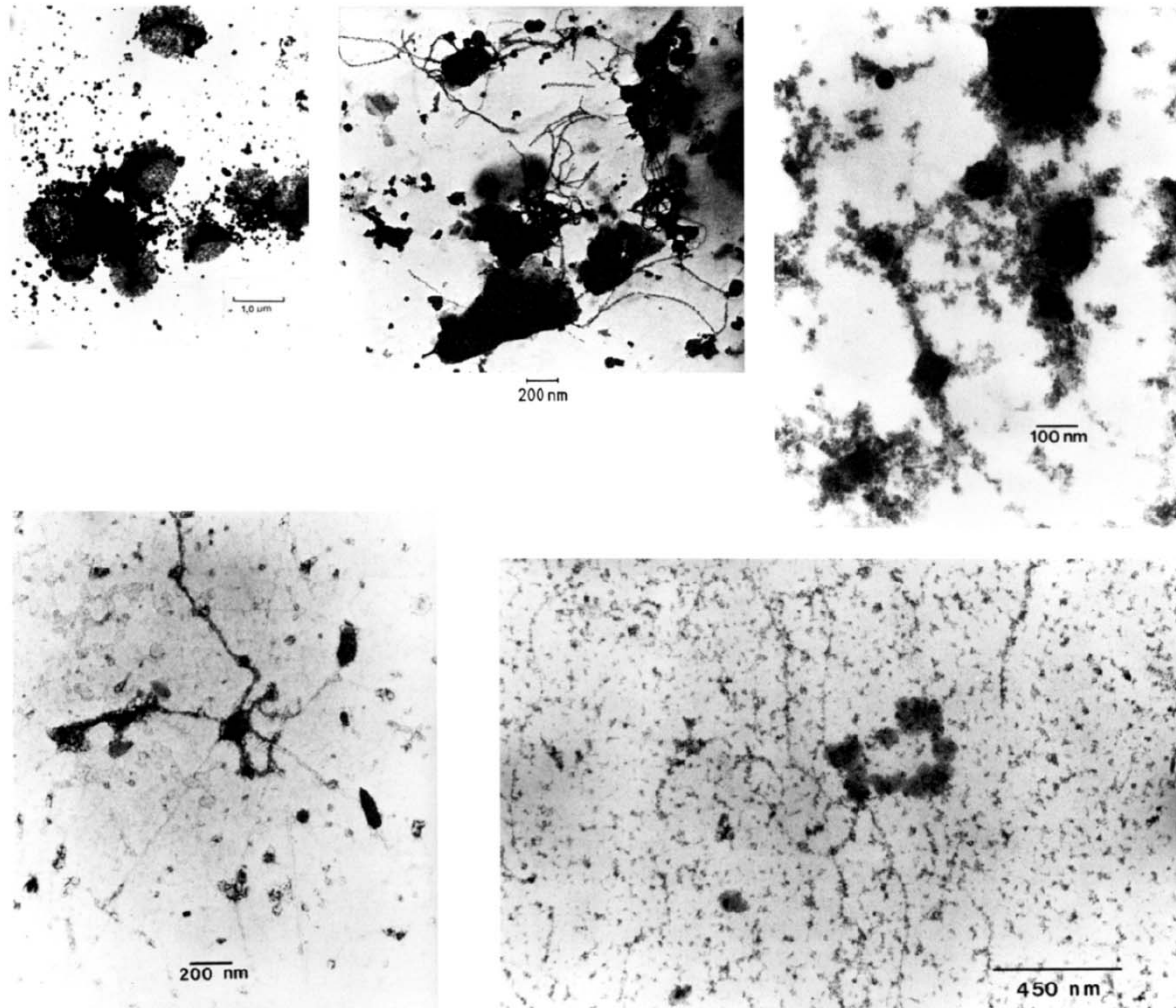
## Co-transport of pollutants



Major types of aggregates formed in the three-colloidal component system: FC (or AROM) ) small points; IC ) circles; RB ) lines. Both FC and polysaccharides can also form gels, which are represented here as gray areas into which IC can be embedded.



## Typical examples of colloidal materials in a eutrophic lake observed by TEM.

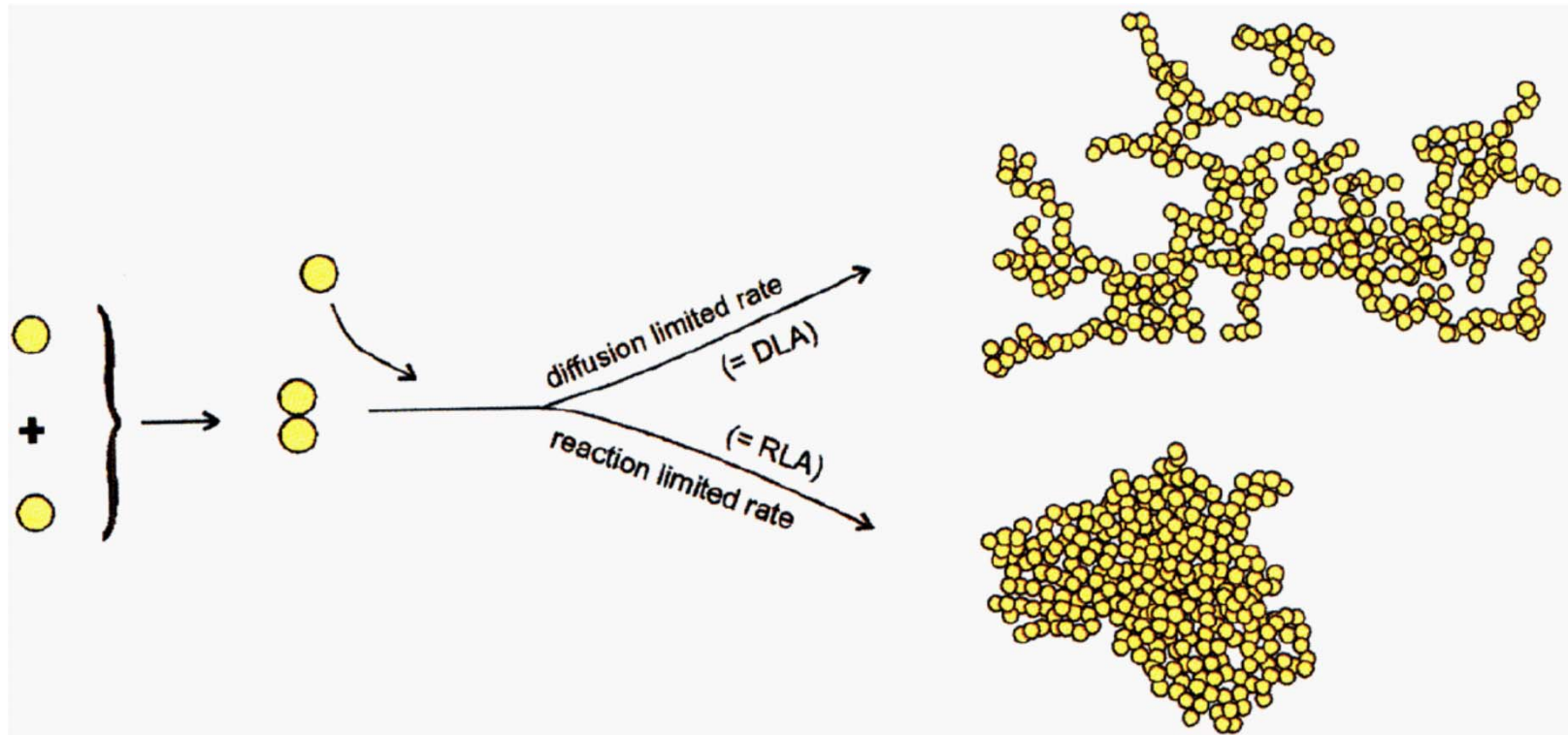


Buffle et al.,

The importance of aggregations in particular between inorganic colloids and organic macromolecules.

Top left: Spores (large spheres) covered and glued together by iron oxyhydroxide globules (small dark globules) formed at the oxic-anoxic interface of the lake. Top middle: Inorganic colloids, in particular clay (large angular particles) and iron oxyhydroxide globules, aggregated together by a mesh of organic filaments. Top right: Inorganic Si-rich colloids (larger dark particles) aggregated in a looser matrix of organic material. Bottom left: Inorganic microcolloids bound together by rather rigid fibrillar material. Bottom right: Soil-derived fulvic compounds aggregated together in slightly larger entities as well as with much larger fibrillar material. At the center, very small iron hydroxide globules in aggregates of fulvics.

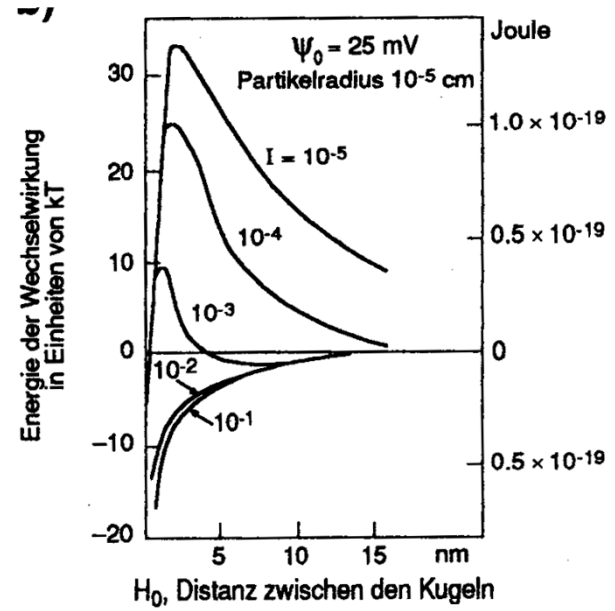
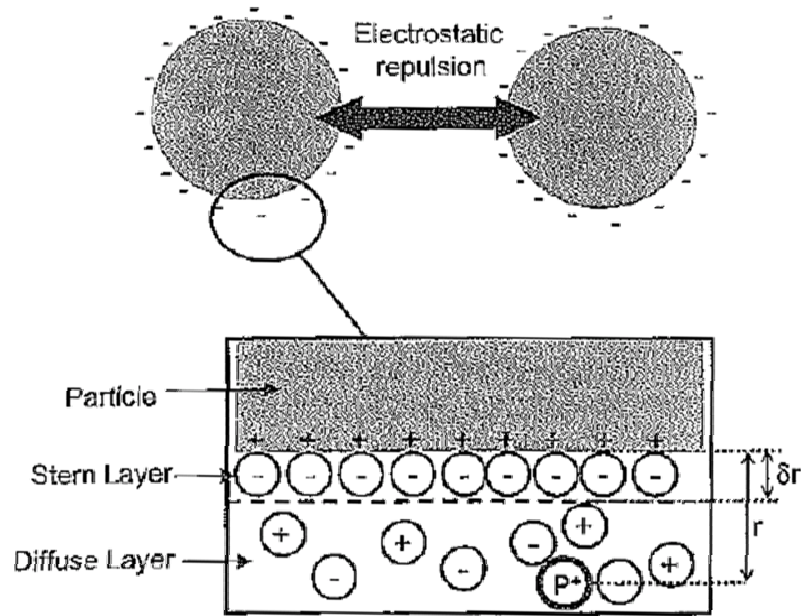
A **diffusion-limited aggregation process (DLA)** and a **reaction-limited aggregation process (RLA)** leading to aggregates of either low fractal dimension (loose aggregate) or higher fractal dimension (denser aggregate), respectively



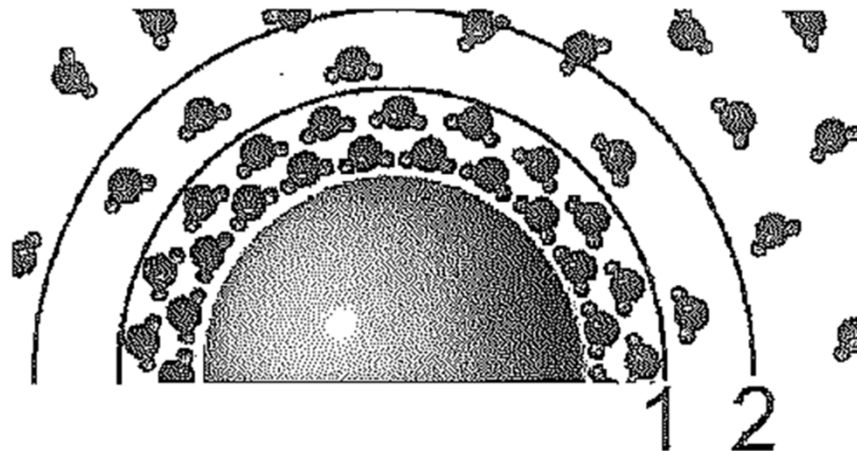
	DLA	RLA
Energy barrier	Absence or primary minimum	Secondary minimum
Type	Reversible	Irreversible
Collision efficiency	1	<1
Aggregation rate	Rapid (Kd)	Slow (KR)
Fractal dimension	~1.8	~2.3



# Electrostatic stabilization of NPs



## Non-DLVO interactions – Hydration effect



e.g. clay minerals

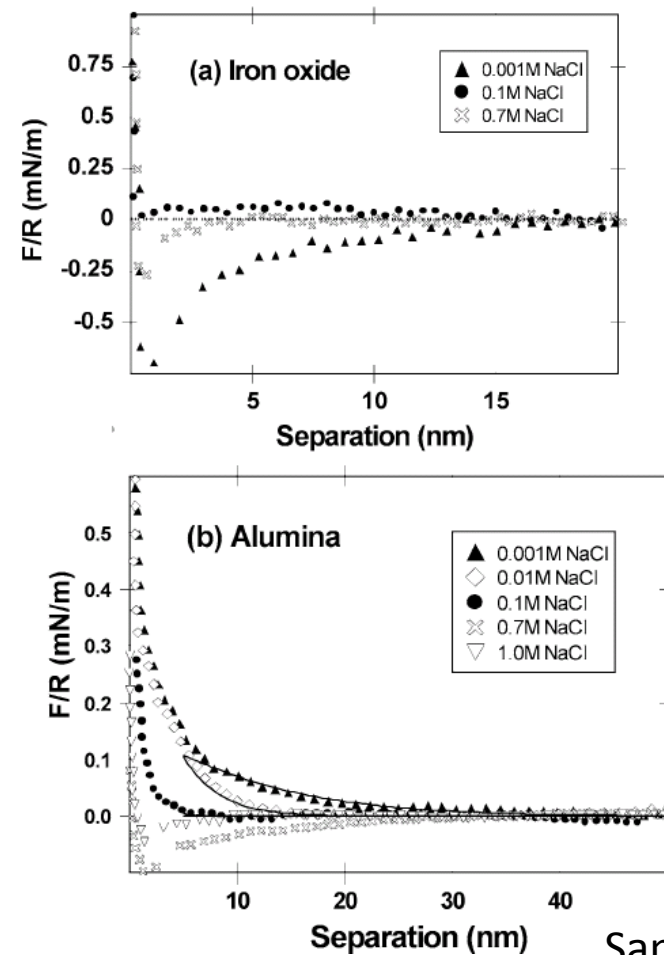
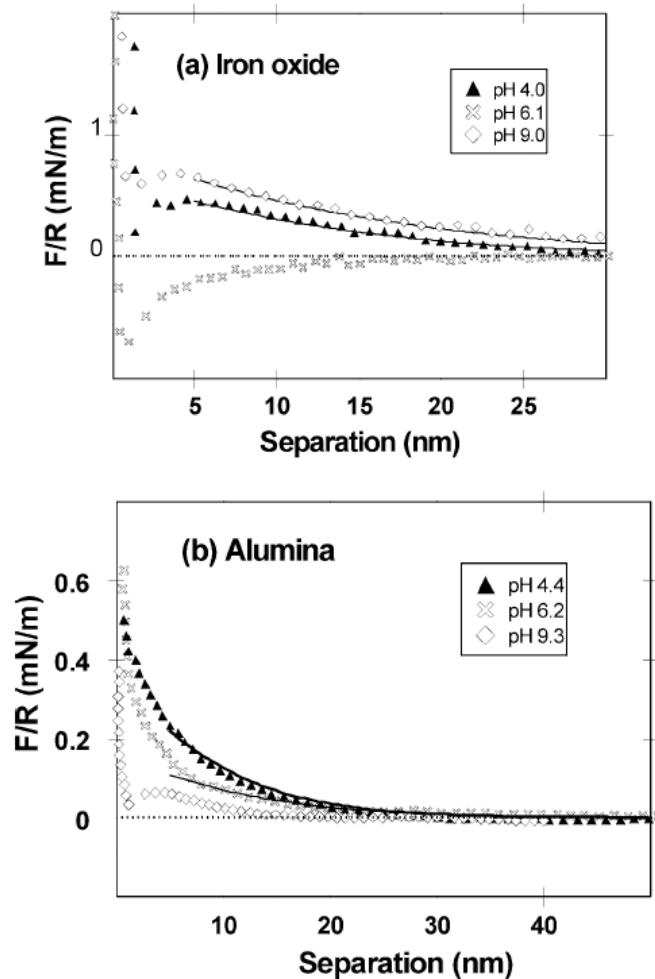
(P. Christian in Lead & Smith)

$$\frac{F_{VDW}}{R} = \frac{A}{6D^2}$$

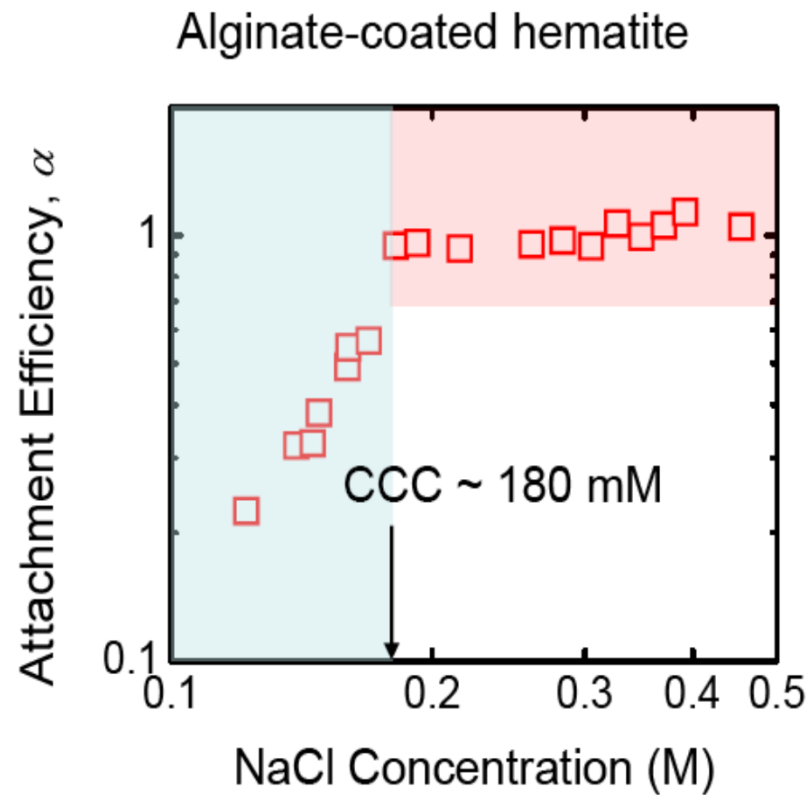
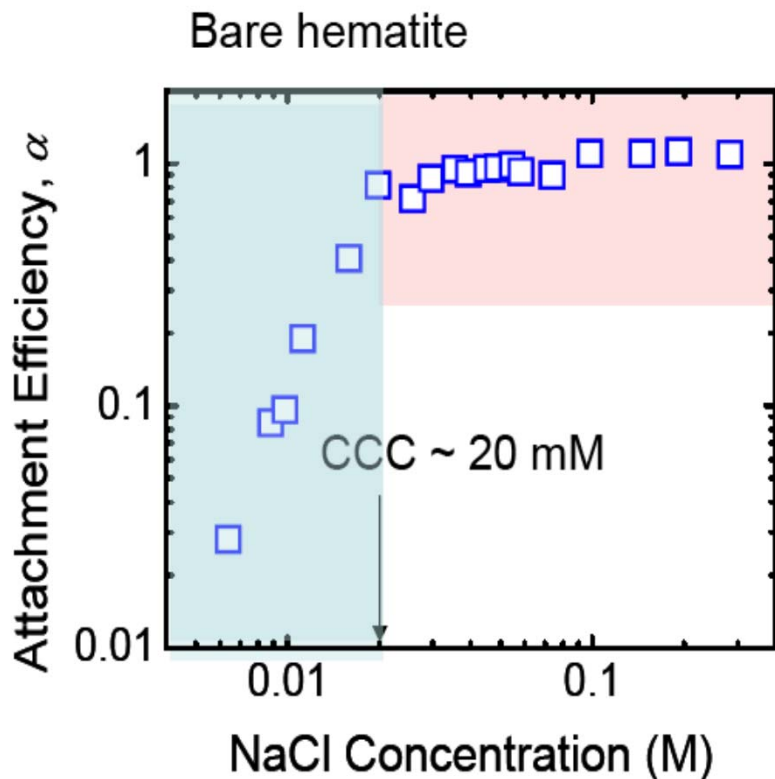
The **van der Waals force ( $F_{VDW}$ )** was calculated using the equation where R is the sphere radius, D is the separation distance between the surfaces, and A is the Hamaker constant.

**Left: pH dependence** of the normalized force (F/R) as a function of surface separation for (a) iron oxide-coated silica and (b) alumina surfaces in 0.001 M NaCl solution. The solid lines show forces calculated from DLVO theory

**Right: ionic strength dependence**



# Aggregation behavior of hematite (70 nm) in presence of DOM



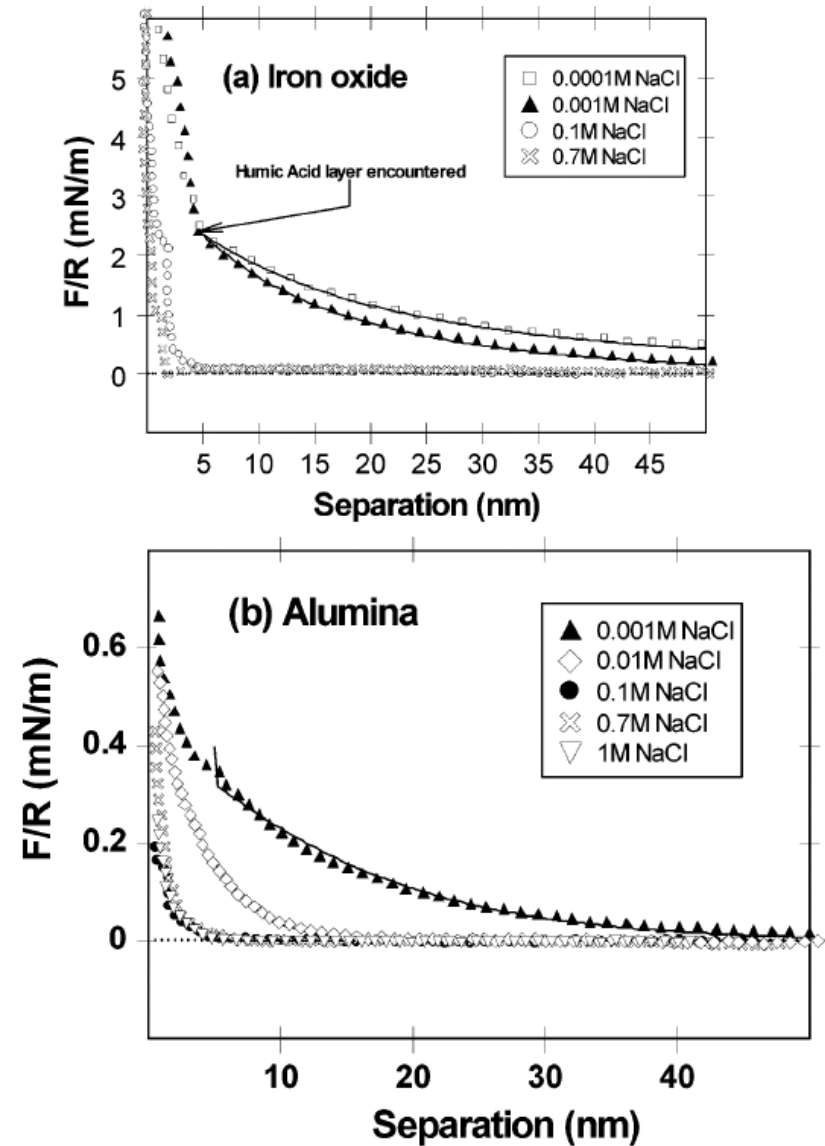
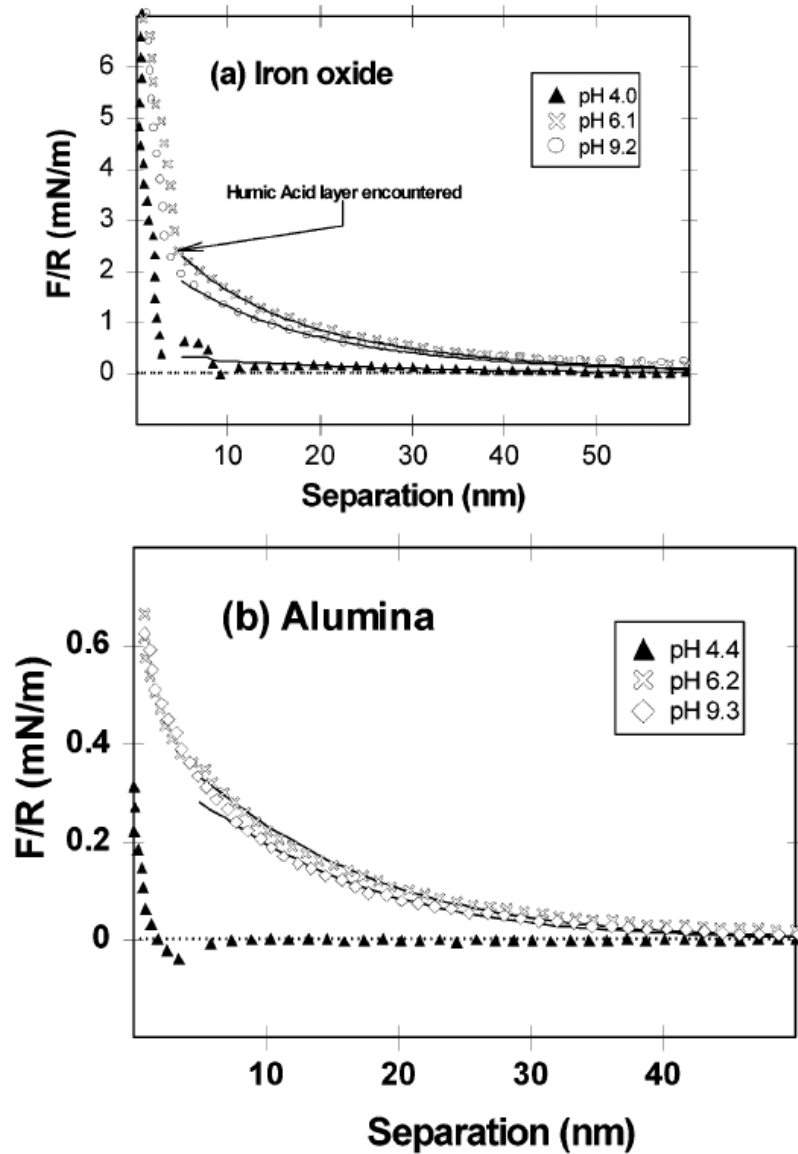
CCC (hematite)  $\ll$  CCC (alginate-hematite)  $\rightarrow$  Steric stabilisation



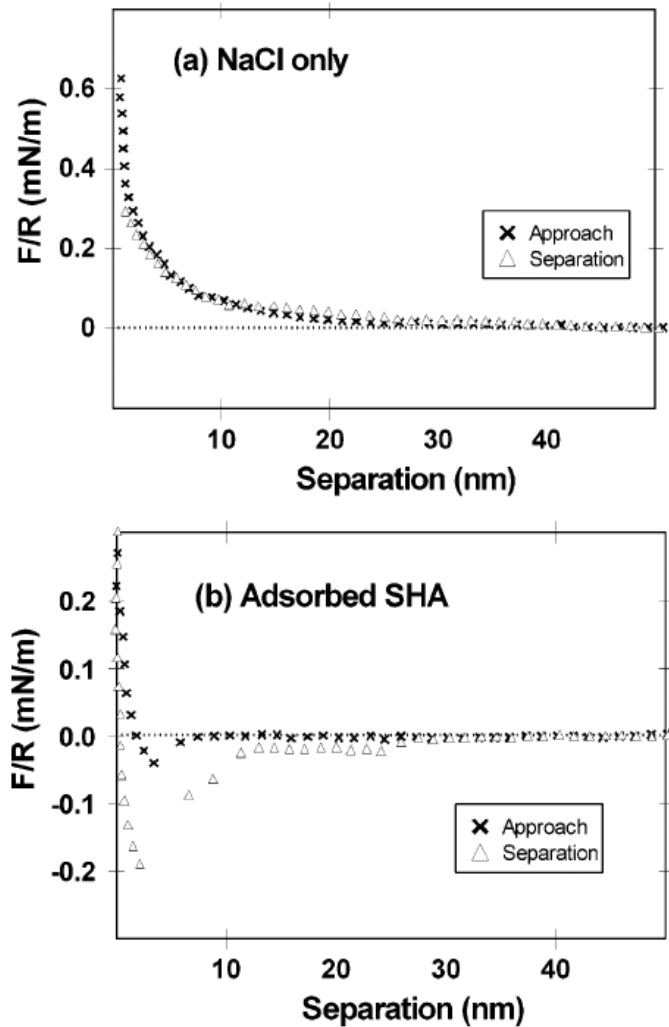
Left: pH dependence of the **normalized force (F/R)** in 0.001 M NaCl as a function of surface separation **after adsorption of HA**: (a) iron oxide and (b) alumina surfaces. Solid lines are calculated from DLVO theory

Sander et al, 2004

Right: ionic strength dependence



Normalized force ( $F/R$ ) as a function of surface separation for both **approach and separation** for alumina surfaces in 0.001 M NaCl (a) pH 6.2 with no HA adsorbed and (b) pH 4.2 with HA adsorbed.



Normalized force ( $F/R$ ) as a function of surface separation for both **approach and separation** for alumina surfaces with adsorbed HA at pH 6 in 0.01 M **CaCl<sub>2</sub>** solution (symbols) and 0.01 M NaCl solution (dashed and dotted lines).

